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STUDY OF THE CRITICAL BEHAVIOUR OF THE MAGNETIZATION AND ELECTRICAL RESISTIVITY IN CUBIC La(Fe, Si)$_{13}$ COMPOUNDS

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The magnetic properties of the cubic $NaZn_{13}$ type pseudobinary compounds $La(T_xSi_{1-x})_{13}$ were studied for T = Fe, Co and Ni in the temperature range 4.2–300 K. ^{57}Fe Mössbauer spectroscopy was performed on $LaFe_{11}Si_2$ and ^{57}Fe-doped $LaCo_{11}Si_2$. The compounds with T = Fe or Co are ferromagnetic, while the compound $LaNi_{11}Si_2$ is a Pauli paramagnet. The critical behaviour around the Curie temperature T_c was studied in $La(Fe_xSi_{1-x})_{13}$ by measuring the temperature dependences of the zero-field susceptibility and the electrical resistivity. The critical exponent γ in the expression $\chi \propto (T - T_c)^{-\gamma}$ was found to be close to 1.38 corresponding to an isotropic Heisenberg ferromagnet. The anomalous critical behaviour shown by electrical resistivity can be explained in terms of lattice softening associated with the Invar effect.

1. Introduction

An intermetallic compound with the cubic $NaZn_{13}$ type of structure is found in only one (La–Co) of the 45 binary systems consisting of a rare earth element and one of the metals Fe, Co or Ni [1]. The compound $LaCo_{13}$ is strongly ferromagnetic with a saturation moment equal to $1.6\mu_B$/Co and a Curie temperature slightly below 1300 K. Kripyakevich et al. [2] showed that the cubic $NaZn_{13}$ type of structure can also be stabilized in other binary rare earth transition metals systems (R–T) by substituting Si for part of the transition metal T in RT_{13}. In the present investigation we have studied the magnetic properties of compounds of the type $La(Fe_xSi_{1-x})_{13}$ with x between 0.8 and 0.9. It will be shown that compounds of this series have characteristics [3] usually encountered in Invar alloys. The anomalous behaviour associated with the Invar problem remains one of the most important and interesting fields of modern magnetism since the Invar problem is closely related to the origin of ferromagnetism in transition metals and their alloys [4,5]. For this reason we have studied the critical behaviour of the $La(Fe_xSi_{1-x})_{13}$ system near the Curie temperature T_c by measuring the low field ac susceptibility and the electrical transport properties. For purposes of comparison, we have also investigated the magnetic properties of the corresponding Co and Ni compounds and we obtained additional information on the magnetic properties by means of ^{57}Fe Mössbauer spectroscopy.

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2. Experimental

Samples of the compounds $La(Fe_xSi_{1-x})_{13}$, $La(Co_xSi_{1-x})_{13}$ and La $Ni_{11}Si_2$ were prepared by means of argon arc melting of the appropriate amounts of the starting materials. The purity of the starting materials was better than 99.9%. After arc melting the samples were vacuum annealed for about 10 days at 900°C. Subsequently the samples were investigated by means of X-ray diffraction. Single phase samples of the cubic $NaZn_{13}$ type of structure were obtained only in a limited concentration region between $x = 0.88$ and 0.81 for $La(Fe_xSi_{1-x})_{13}$ and $x \geq 0.81$ for $La(Co_{1-x}Si_x)_{13}$ (for $La(Ni_{1-x}Si_x)_{13}$ only a single concentration was studied).

The magnetic properties of these samples were determined by means of an adaptation of the Faraday method in the temperature range 4.2–300 K using magnetic field strengths up to 1.8 T. For several of the $La(Fe_xSi_{1-x})_{13}$ compounds the temperature dependence of the low field (0.1 mT) ac susceptibility was determined as well. These measurements were performed with a sensitive mutual inductance technique operating at a frequency of 118 Hz with a driving field less than 0.1 mT.

The electrical resistivity was measured on samples of dimensions of $1 \times 1 \times 15$ mm^3 cut by means of spark erosion. We used a standard four probe technique with a dc current of 10 mA constant to a few ppm. The voltage determination was accurate to about 2 parts in 10^5. The error of the measured absolute resistivity was about 2% owing to uncertainties in the sample dimensions. The temperature was varied stepwise and determined to within 0.2% by means of calibrated Ge and Pt resistors.

The ^{57}Fe Mössbauer spectra were obtained with a standard constant-acceleration type spectrometer in conjunction with a ^{57}Co–Rh source. The hyperfine fields were calibrated by means of the field in α-Fe_2O_3 at 295 K (51.5 T).

3. Experimental results

Examples of the magnetization measurements are displayed in fig. 1 for the two compounds

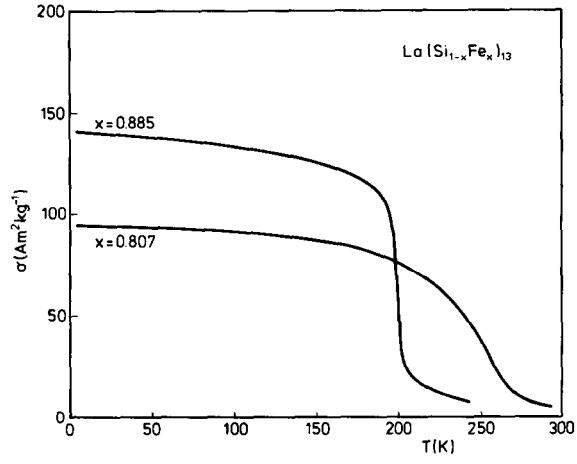

Fig. 1. Temperature dependence of the magnetization in $LaFe_{11.5}Si_{1.5}$ ($x = 0.885$) and $LaFe_{10.5}Si_{2.5}$ ($x = 0.807$) measured in a field of 3 kOe.

corresponding to the boundaries of the concentration region in which the cubic $NaZn_{13}$ type structure is formed in samples of the type $La(Fe_xSi_{1-x})_{13}$. The behaviour found for the samples of intermediate concentration are quite similar. In all cases the shape of the magnetization versus temperature curve was typically that of a ferromagnetic compound. The extreme sharpness of the paramagnetic-to-ferromagnetic transition is more clearly seen from the measurements of the near zero-field susceptibility. As an example we

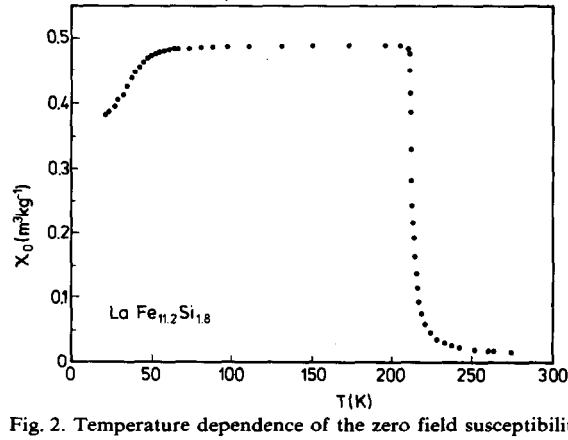

Fig. 2. Temperature dependence of the zero field susceptibility χ_0 in $LaFe_{11.2}Si_{1.8}$.

Table 1
Magnetic properties of various pseudo-binary compounds of the cubic $NaZn_{13}$ structure

$La(Fe_xSi_{1-x})_{13}$	x	T_c (I)	μ_s (μ_B/Fe)
$LaFe_{11.5}Si_{1.5}$	0.885	198	2.08
$LaFe_{11.2}Si_{1.8}$	0.861	211	–
$LaFe_{11.1}Si_{1.9}$	0.854	219	–
$LaFe_{11.0}Si_{2.0}$	0.846	230	1.95
$LaFe_{10.9}Si_{2.1}$	0.838	234	–
$LaFe_{10.8}Si_{2.2}$	0.831	245	–
$LaFe_{10.5}Si_{2.5}$	0.807	262	1.85
$LaCo_{13}$	1.0	1290	1.58
$LaCo_{11.5}Si_{1.5}$	0.885	–	1.29
$LaCo_{11}Si_2$	0.846	–	1.14
$LaCo_{10.5}Si_{2.5}$	0.807	–	0.88
$LaNi_{11}Si_2$	$\chi = 2.5\times10^{-7}$ m^{3}kg^{-1}		

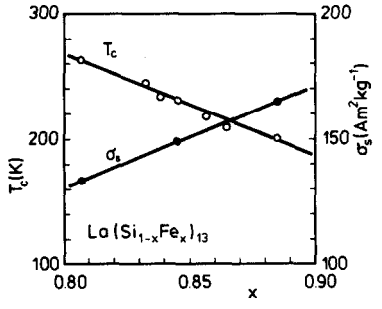

Fig. 3. Concentration dependence of the Curie temperature T_c and saturation magnetization σ_s in $La(Fe_xSi_{1-x})_{13}$.

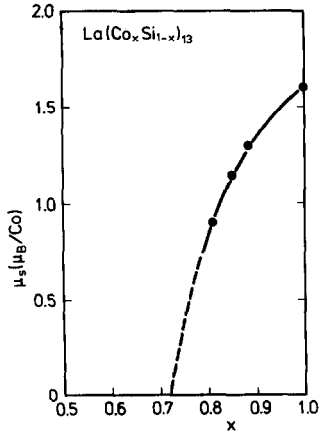

Fig. 4. Concentration dependence of the saturation moment μ_s in $La(Co_xSi_{1-x})_{13}$.

show in fig. 2 the results obtained for $LaFe_{11.2}Si_{1.8}$. The values of the saturation magnetization at 4.2 K (μ_s) and the values of the Curie temperature (T_c) are listed for the various compounds in table 1. These quantities have been plotted as a function of concentration in fig. 3. The saturation magnetization (σ_s) and the corresponding saturation moment (μ_s) increase linearly with x (see fig. 3). Extrapolation to $x = 1$ would lead to a saturation moment of $2.3\mu_B$/Fe for the hypothetical compound $LaFe_{13}$. A linear extrapolation may, however, not be justified as can be inferred from the results shown for the corresponding Co compounds in fig. 4. Note that in this case the Si-free compound does exist ($LaCo_{13}$). Similar to $La(Fe_xSi_{1-x})_{13}$ there is no Si-free compound in the series $La(Fe_xSi_{1-x})_{13}$. The compound $LaNi_{11}Si_2$ is a Pauli paramagnet with $\chi = 2.5\times10^{-7}$ m^{3}kg^{-1}. Consequently no other compounds of this series were investigated. Results of the magnetic measurements on the Co- and Ni compounds have also been included in table 1.

Mössbauer spectroscopy was performed on the compounds $LaFe_{11}Si_2$ and $LaCo_{11}Si_2$. For this purpose the latter compound was doped with a few percent of iron enriched (95%) in the isotope ^{57}Fe. The spectra obtained 4.2 K are shown in fig. 5. The effective hyperfine field in $LaFe_{11}Si_2$

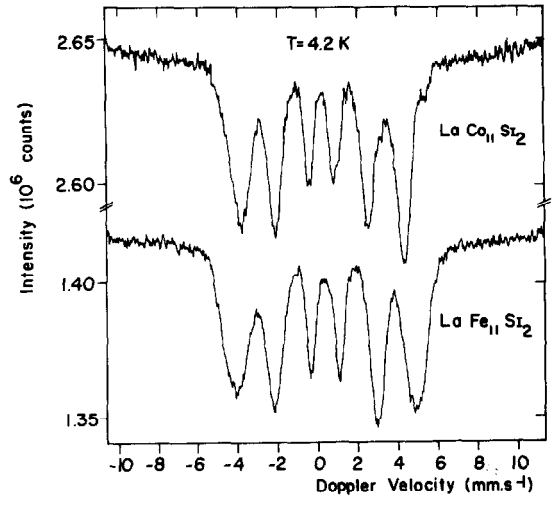

Fig. 5. Mössbauer spectra at 4.2 K for $LaFe_{11}Si_2$ and $LaCo_{11}Si_2$. The latter compound was doped with a few percent of enriched ^{57}Fe.

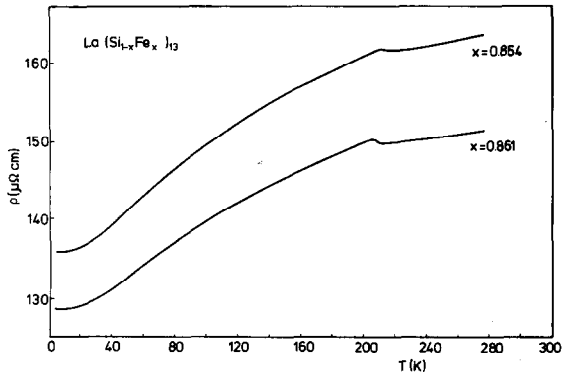

Fig. 6. Temperature dependence of the electrical resistivity ρ in $LaFe_{11.2}Si_{1.8}$ ($x = 0.861$) and $LaFe_{11.1}Si_{1.9}$ ($x = 0.854$).

equals $H_{eff} = 28.0$ T. In Fe-doped $LaCo_{11}Si_2$ it is slightly smaller, $H_{eff} = 25.5$ T.

Results of the resistivity measurements $\rho(T)$ are shown in figs. 6 and 7. Particularly in the compounds with $x = 0.861$ ($LaFe_{11.2}Si_{1.8}$) and $x = 0.854$ ($LaFe_{11.1}Si_{1.9}$) there is a pronounced cusp associated with the paramagnetic to ferromagnetic transition. An impression of the sharpness of this discontinuity near T_c can be obtained from fig. 8 where we have plotted the temperature dependence of $d\rho/dT$ in the region close to T_c. The Curie temperatures of the various compounds determined by the ac susceptibility are indicated by arrows. The results depicted in fig. 9 show the temperature dependence of $d\rho/dT$ in one of the

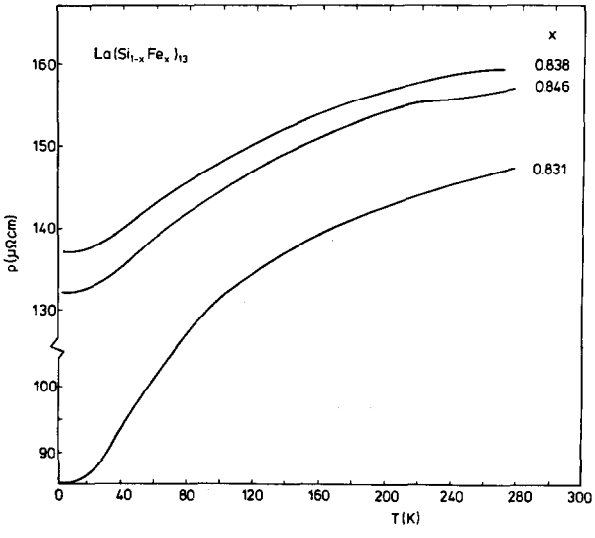

Fig. 7. Temperature dependence of the electrical resistivity ρ in $LaFe_{10.9}Si_{2.2}$ ($x = 0.838$), $LaFe_{11.0}Si_{2.0}$ ($x = 0.846$) and $LaFe_{10.8}Si_{2.2}$ ($x = 0.831$).

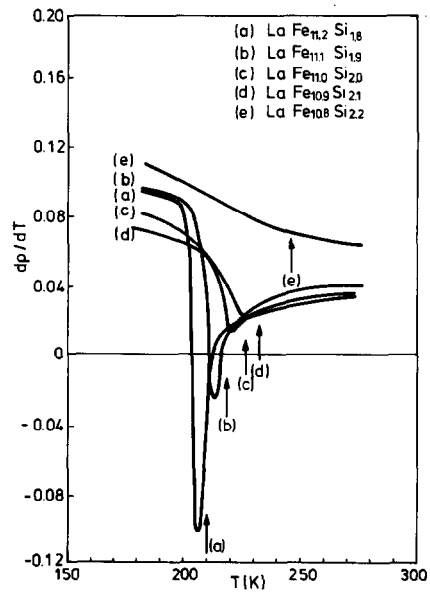

Fig. 8. Temperature dependence of the resistivity derivative $d\rho/dT$ in several $La(Fe_xSi_{1-x})_{13}$ compounds near T_c. The position of T_c is indicated by means of arrows.

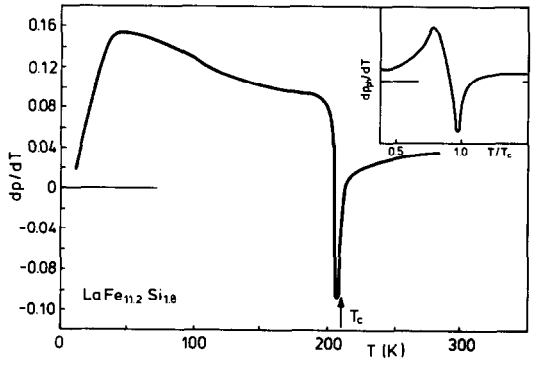

Fig. 9. Temperature dependence of the derivative $d\rho/dT$ in $LaFe_{11.2}Si_{1.8}$ in the range 4.2–300 K. The position of T_c is indicated by an arrow. The inset shows the calculated temperature dependence of the derivative $d\rho/dT$ of the phonon part ρ_{ph} of the electrical resistivity in the compound Fe_3Pt (taken from Viard and Gavoille [15]).

compounds of the series over a more extended temperature range.

4. Discussion

4.1. Composition and stability

The cubic $NaZn_{13}$ structure encompasses two different Zn sites occurring in a ratio 1 : 12. In Wyckoff notation these sites are designated by the symbols 8(b) and 96(i), each unit cell comprising 8 formula units $NaZn_{13}$. On the grounds of the crystal structure one would have expected compound formation to occur around the composition $LaFe_{12}Si$ rather than around $LaFe_{11}Si_2$. Evidently the occurrence of two different Fe positions is of minor importance. Here one has to consider that the heat of alloying between La and Fe is positive which follows from the fact that there exist no stable La–Fe intermetallics. Thus a minimum amount of Si will be required to create a pseudobinary compound with a negative heat of formation and having, in addition, a suitable structure to accommodate the sizes of all of the three constituent atomic species. This is probably the reason why a composition with a higher Si content than $LaFe_{12}Si$ is favoured. When the Si content becomes too high other structures of different composition become favoured, and this determines the phase boundary of the $NaZn_{13}$ type structure at the high Si concentrations side. Note that in the case of $La(Co_xSi_{1-x})_{13}$ only this latter phase boundary exists. At the low Si concentration side there is complete solubility up to $x = 1$. Since the heat of alloying for La–Co is already negative a minimum Si concentration for compound formation is not required as evidenced by the existence of $LaCo_{13}$. In the case of $La(Ni_xSi_{1-x})_{13}$ the situation is not much different from that of the Fe-base compounds. The phase $LaFe_{13}$ is not stable with respect to the pure 3d metal and La, whereas the phase $LaNi_{13}$ is not stable with respect to the pure 3d metal and the Haucke phase $LaNi_5$. In the Ni case, too, additional stabilization is required by substitution of Si for Ni in $La(Ni_xSi_{1-x})_{13}$. It follows from the above discussion that from the crystallographic point of view (preferred site occupancy) neither of the two compositions $LaT_{12}Si$ and $LaT_{11}Si_2$ represents anything special. It is very probable therefore that the substitution of Si proceeds in a more or less random way. The associated distribution of hyperfine parameters is reflected in some broadening of the Mössbauer lines, as can be seen from fig. 5.

4.2. Magnetic properties

In a previous investigation [6] of Fe-base intermetallics we compared the ^{57}Fe hyperfine fields with the corresponding saturation moments and found that these quantities are related by the conversion factor 14.5 T/μ_B. Using the data obtained for $LaFe_{11}Si_2$ in the course of the present investigation we find this conversion factor to be equal to 28 $T/1.98\ \mu_B = 14.1\ T/\mu_B$ which is close to the value obtained previously. For the ^{57}Fe-doped compound $LaCo_{11}Si_2$ this factor is much higher (25.5 $T/1.14\ \mu_B = 22.4\ T/\mu_B$). Here one has to take into consideration that the hyperfine field is composed of the core contribution of the Fe atoms and a transferred contribution due to the Co atoms. The former scales to the Fe moments whereas the latter scales to the Co moments so that the conversion factor is not a very meaningful quantity.

Keeping in mind that, owing to the distribution of local environment of the 3d atoms, there will be a distribution of exchange fields in $La(Fe_{1-x}Si_x)_{13}$, it is surprising that the paramagnetic-to-ferromagnetic transitions in these compounds are so extremely sharp (see for instance, fig. 2). In fact, it appears that these compounds behave as textbook type ferromagnets where for $T > T_c$ the susceptibility can be represented by [7]

$$\chi = \text{const} \times (T - T_c)^{-\gamma}.$$

As can be seen from fig. 10 a linear dependency is obtained when $\log \chi_0$ is plotted versus $\log(T - T_c)/T_c$. The slope of the straight line corresponds to $\gamma = 1.38$ for $LaFe_{11.2}Si_{1.8}$ and to $\gamma = 1.37$ for $LaFe_{10.8}Si_{2.2}$. The value of γ for Fe metal equals 1.33. These experimental values of the critical exponent γ may be compared with theoretical values, being equal to $\gamma = 1.24$ for the three-dimensional Ising model and $\gamma = 1.38$ for the isotropic Heisen-

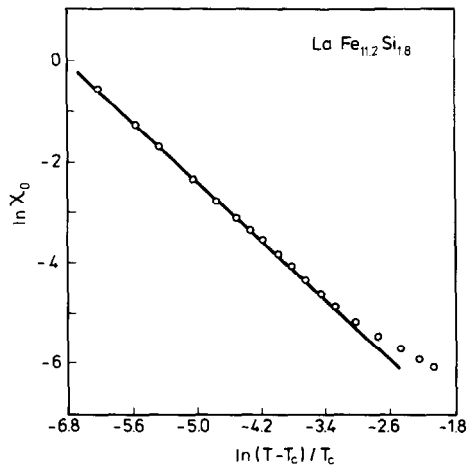

Fig. 10. Log χ_0 plotted versus $\log(T - T_c)/T_c$ for the compound $LaFe_{11.2}Si_{1.8}$.

berg model. There is excellent agreement between the experimental values of the compounds studied here and the values derived for the isotropic Heisenberg model. On the grounds of the cubic crystal structure one would expect the compounds $La(Fe_xSi_{1-x})_{13}$ to show indeed a preference for a behaviour corresponding to the isotropic Heisenberg model.

It can be seen from table 1 and fig. 3 that the magnetic ordering temperature in the compounds $La(Fe_xSi_{1-x})_{13}$ depends on concentration in a rather peculiar way. The moment per Fe atom increases with increasing Fe concentration and behaves in accordance with expectations. The increase in Fe moment is seen, however, to be accompanied by a decrease of the Curie temperature. Such features have been associated with the anomalous thermal expansion below T_c found in Invar type alloys [3]. Invar type anomalies of the thermal expansion were also observed in the Fe-base compounds investigated the course of this study and will be reported separately [8].

4.3. Electrical resistivity

It was shown at the end of section 3 that several of the $La(Fe_xSi_{1-x})_{13}$ compounds give rise to a cusp like anomaly near T_c in the dependence of the resistivity on temperature. Attempts were made by De Gennes and Friedel [9] to explain such anomalies in terms of spin fluctuations although these authors failed to reproduce the sharpness of the anomaly. Using the same physical ideas Fisher and Langer [10] were more successful in this respect. If the anomaly found in the present compounds were due to short-range spin fluctuations at a ferromagnetic critical point one would expect, according to Fisher and Langer, a sharp maximum of $d\rho(T)/dT$ lying above the Curie temperature. As can be seen from the results shown in fig. 8 this is not the case. Apparently the Fisher and Langer model is not suited in explaining the anomalies found in the compounds studied here. Somewhat better agreement is found with the model proposed by Kim [11] where a sharp maximum of $d\rho/dT$ is expected to occur at the transition [11,12].

It is well known that the elastic constants behave very anomalously below T_c in the case of Invar alloys (see, for instance, refs. [13,14]). This has lead Viard and Gavoille [15] to propose that a substantial portion of the critical ρ-behaviour around T_c originates from the critical scattering of the conduction electrons by phonons coupled to the spin fluctuations by means of the Invar effect. The total resistivity can be written as $\rho = \rho_{res} + \rho_{sp} + \rho_{ph}$ where the abbreviations "res", "sp" and "ph" refer to the residual, spin and phonon part of the resistivity, respectively. Apart from the Fisher and Langer type anomaly contained in ρ_{sp} one may expect a further anomaly due to ρ_{ph}, whose temperature dependence can be represented by means of $\rho_{ph} = (A/B)(1 - g\omega)T$. Here A is a constant, B the bulk modulus, g a constant close to 1 and ω the lattice expansion. Using experimental data for B and ω in the Invar type compound Fe_3Pt, Viard and Gavoille calculated the temperature derivative of the phonon part for this compound. Although the compound Fe_3Pt is different from the compounds $La(Fe_xSi_{1-x})_{13}$, there are points of similarity comprising the high Fe concentration and the cubic symmetry. Due to lack of more appropriate data we have therefore reproduced the results of Viard and Gavoille in the inset of fig. 9. Comparison with the data shown in the main part of the figure makes clear that the $d\rho_{ph}/dT$ behaviour obtained by these authors has essentially the same features as those observed in

the compounds investigated here. One may also notice that, contrary to the Fisher and Langer result, the anomaly occurs at the low-temperature side of the transition temperatures. Since $d\rho_{ph}/dT \propto \omega/B$ this feature can be traced back to the bulk modulus B which exhibits a very sharp minimum in the region below T_c, corresponding to a decrease of the order of 50%.

5. Concluding remarks

The fact that relatively small amounts of Si are able to stabilize the cubic $LaFe_{13}$ phase in the La–Fe systems shows that the heat of alloying is only slightly positive in the Fe-rich portion of the La–Fe system, which agrees with model predictions [16].

It has been shown that the compounds of the type $La(Fe_xSi_{1-x})_{13}$ show strong critical behaviour in their temperature dependence of the magnetization susceptibility and resistivity. A ferromagnetic state occurs which has a susceptibility critical exponent corresponding to that found in isotropic, 3-dimensional Heisenberg ferromagnet. The anomalous critical behaviour of the resistivity was explained in terms of lattice softening near the Curie temperature associated with the Invar anomaly as proposed for Fe_3Pt by Viard and Gavoille. The results obtained here strongly support the view of Viard and Gavoille since in the compounds $La(Fe_xSi_{1-x})_{13}$ the presence of soft modes which sometimes precede the martensitic transformations in Fe_xPt_{1-x} can be taken to be absent.

Acknowledgements

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